

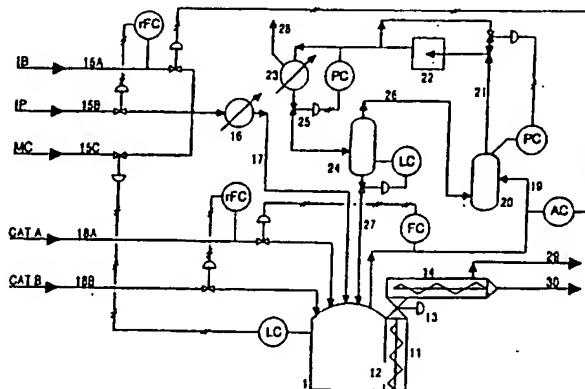
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/IT93/00033 (22) International Filing Date: 13 April 1993 (13.04.93) (30) Priority data: MI92A000914          15 April 1992 (15.04.92)          IT (71)(72) Applicants and Inventors: BRUZZONE, Mario [IT/IT]; Via Kennedy, 25, I-20097 San Donato Milanese (IT). GORDINI, Silvano [IT/IT]; Via Pascoli, 36/A, I-20097 San Donato Milanese (IT). (74) Agents: KLAUSNER, Erich et al.; Ufficio Internazionale Brevetti, Ing. C. Gregorj S.p.A., Via Dogana, 1, I-20123 Milan (IT).	(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  Published <i>With international search report.          Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	

(54) Title: NEW PROCESS FOR BUTYL RUBBER PRODUCTION



## (57) Abstract

This invention relates to a continuous slurry process for the production of Butyl Rubber (IIR) and to the devices thereof. The new process allows substantial energy and investment saving vis-à-vis conventional processes. In the new process the polymerization is performed at -50 °C instead of -100 °C, by using special catalysts. The polymerization heat is removed by allowing the reaction medium to boil at reduced pressure, instead of exchanging it through the reaction walls. The polymerization reactor is a tri-phasic reactor, i.e. it contains a polymer dispersed phase, a liquid phase (composed of monomers and methylchloride), and a vapor phase. The reactor is designed in order to: i) homogenize the liquid phase in every point of the reactor; ii) convey (to "skim") the formed polymer particles across the reactor toward the slurry outlet; iii) separate the vapor phase on the upper part of the reactor (reactor dome) where the vapors are taken away by a vapor outlet. The slurry discharged by the reactor is taken away by a vertical extruder adjacent and connected to the reactor by a slit. The extruder screw conveys and concentrates by compression the slurry, whereas the liquid phase flows back to the reactor. In this invention, the combination of the abovesaid critical characteristics allows the production energy of IIR to be abated by more than 20% and the investment by more than 30 %. The process scheme is shown in fig. 1.

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- 1 -

DESCRIPTIONNEW PROCESS FOR BUTYL RUBBER PRODUCTION

This invention relates to a new process for production of isobutene polymers and co-polymers, and to the devices thereof.

In particular, the invention relates to the production of high MW isobutene-isoprene copolymers, known as Butyl Rubber or "IIR".

IIR is known for about 50 years (U.S. 2356128 and U.S. 2356130). It finds application as a low gas diffusion and oxidation resistant rubber. IIR is commercially produced in the presence of cationic catalysts, also known as Friedel-Craft catalysts, at extremely low temperatures (e.g. 173 K°), in a reaction medium of methylchloride. Unlike to its monomers, IIR is not soluble in methylchloride, so that a polymer slurry is formed. Details on this technology are available in the literature (C. Whitby Synthetic Rubber, Chapt.24 J. Wiley & Sons and Kirk Othmer Encyclopedia of Chem. Technol., Butyl Rubber).

Even if the present IIR processes are still valid, they show important drawbacks. These drawbacks can be summarized as follows:

- i) the energy consumption of the process is very high
- ii) the plant investment cost is also very high
- iii) the quality constancy control is difficult

In more detail :

i) The high energy consumption is due to a series of cooling cycles for supplying the process with the necessary frigories at 173 K°. As an order of magni

- 2 -

5 tude the energy cost of cooling cycles can be as high as 75% of the total energy requirement.

10 ii) The investment cost of a IIR plant is also very high. Beside the cost of the mentioned cooling cycles, which can be as high as 35% of the total investment, the polymerization reactors are very expensive. In fact their design is very complex and they are built with expensive criogenic materials. The investment cost is exacerbated by the fact that every 2-30 reactors in operation a supplementary stand-by reactor is needed, 15 since the internal heat exchangers fowling imposes a rather frequent reactor shut-down for cleaning.

20 iii) The IIR quality depends on its MW, and in turn MW depends on polymerization temperature. The above mentioned reactor fowling is conducive to a temperature increase inside the reactor. Consequently, the operating life of the reactor lasts for a few ten hours. This fact has an impact on IIR quality constancy.

25 In order to overcome the aforementioned drawbacks, several solutions have been proposed and patented. However these solutions were not solving the basic problems of IIR process, or were not pratically applicable.

30 Among the relevant proposed solutions, the use of new catalyst systems, called by some researches "syncatalysts" has been put forward about 20 years ago.

35 The syncatalysts allowed in principle to obtain high MW IIR even at a temperature as high as 223K°, vis a vis the 173K° of the conventional processes. However, the pratical use of syncatalysts has been ruled out by the worsening of the already critical problem of reactor

- 3 -

fowling.

More recently a new IIR process (U.S. 4714747) has been patented in which syncatalysts are used without meeting heat exchange problems due to reactor fowling.

According to U.S. 4714747, monomers and reaction medium are fed into a double screw. self cleaning extruder. Inside this extruder the reactant fluids followed a peculiar fluidodynamics known as "plug flow". The boiling of reaction medium inside the extruder was avoiding the need of a heat exchange through the reactor walls. However, as point out in U.S. 4714747, the double screw extruder was compacting the polymer in a "viscous and sticky mass" which hampered the vapor separation and, consequently, the reactor temperature control.

In conclusion, also this solution was difficult to put in practice.

All the aforementioned drawbacks are overcome by the process and by the devices of this invention, in which are contemporarily present all the following critical characteristics:

1) The polymerization is performed at temperatures between 208 and 288K°, in the presence of syncatalysts, whose two (or more) components are fed directly and separately to the polymerization reactor.

2) The polymerization heat is removed by allowing the reaction medium to boil inside the reactor, and maintaining the reactor content as a low viscosity polymer slurry.

3) The polymerization reactor is designed in order to keep the reactor content as a low viscosity slurry. A coalescence of polymer particles in bigger

- 4 -

and bigger crumbs is avoided, which is conducive to the "viscous and sticky mass" shown in U.S. 4714747. In the reactor of the present invention, the vapors produced by the exothermic polymerization reaction can easily escape from the polymer slurry, owing to its low viscosity, and collect in the reactor dome.

4) The polymerization reactor is designed in order to fulfill other important duties : one is that of homogenizing the liquid phase in every point of the reactor condensed phase, in order to maintain a constant composition of reactants. The second is that of conveying the polymer phase across the reactor, toward the polymer slurry outlet. The third is that of concentrating the polymer slurry discharged by the reactor. The last two duties, which are somewhat recalling certain dairy processes, have been dubbed with the word "skimming".

5) The skimmed slurry flowing from the reactor outlet is concentrated further on in a vertical extruder connected with the reactor. This vertical extruder, referred to as "discharge screw", conveys and presses the solid polymer contained in the slurry upward and "squeezes" the liquid downward (i.e. backward) toward the reactor. In this way, valuable catalyst components, soluble in the reaction medium, are re-fluxed to the reactor for a further utilization.

The details of the process of the present invention and of the devices for its practical application are dealt with herebelow.

#### Polymerization reactor

The reactor is a vertical cylindrical vessel,

- 5 -

equipped with a special stirrer. In fig. 2 a vertical section is shown. The reactor wall is indicated by 1; 2 and 3 are respectively the reactor ceiling and bottom, 4 is the stirrer shaft, 5 is a standing shaft fastened to the reactor bottom, 6 is one of the vertical paddles, moved by shaft 4 to which they are connected by the cross bar 7. The rotating bars 8 intermesh with standing crossbars 9. 10 is an extruder barrel fastened to the reactor, to which it is connected via slit 12. This extruder, equipped with its screw 11, is hereinafter referred to as "discharge screw".

An horizontal reactor section is also shown in fig. 2. The section is along a standing bar 9. In this figure, three paddles 6, one bar 9 and the slit 12 are shown. The three paddles 6 have a peculiar shape and orientation. When they rotate according to the direction indicated by an arrow, the clearance between a point on the reactor wall and the paddle decreases till to a very small clearance.

The reactor is equipped with on inlet for the monomers/polymerization medium mixture, and of two inlets for feeding the catalyst components. The reactor is also equipped with a vapor outlet, placed in the reactor ceiling.

The following description of the reactor operation in a continuous, steady state operation will better explain the function of every reactor fitting.

The reactor operates at constant level of condensed phase (which includes liquid monomers and reaction medium and polymer particles).

IIR particles are continuously formed in the

- 6 -

reactor, and are immediately conveyed by the stirrer across the reactor, toward its peripheric part, where the slurry discharge 12 is placed, with a continuous skimming action.

5           The rather small clearance among moving and standing surfaces of the stirrer/reactor system limits the surfaces fowling, but does not hamper the liquid phase to flow across the clearances. In the way, the liquid phase is homogenized throughout all the reactor.

10           The polymer skimming is performed in the following way: the polymer slurry present in the peripherical part of the reactor is continuously intaken into the rather large clearance between the paddle leading edge and the reactor wall. The liquid phase.

15           can easily flow through the clearance between the paddle rear edge and the reactor wall. On the contrary the polymer particles are "caught" owing to their size. Therefore the slurry concentration in the space between the paddle and the reactor wall increases during the paddles motion. The rear paddle edge squeezes

20           the polymer slurry against the wall for a phenomenon of visco-dynamic pressurization (Z. Tadmor, C. Gogos Principles of Polymer processing Wiley-Interscience Chap. 10), which increases the solid content of the slurry,

25           whereas the liquid is squeezed out. Whenever a paddle 6 passes in front of slit 12, the slurry is pumped through it, toward the discharge screw 11, which carries it up. Therefore, whenever a paddle 6 passes in front of slit 12, the slurry contained in the volume

30           between paddle and wall is cleared out, and is ready to be re-filled by another amount of slurry, coming



from the axial part of the reactor. A step carved in the rear edge of paddles 6 decreases the gap between paddle and wall and increases the skimming efficiency.

At a certain stirrer rotation speed, the  
5 polymer discharged by the reactor in unit time increa  
ses proportionally to the polymer concentration.

At a certain polymer concentration, the poly-  
mer discharged by the reactor in unit time increases  
proportionally to the stirrer rotation speed.

10 Consequently, the above reactor has a built-  
in capacity of controlling the polymer concentration  
inside the reactor. Once a certain value of polymer  
output has been selected, by feeding the catalyst at a  
certain rate, the polymer concentration inside the  
15 reactor cannot overcome an upper threshold limit,  
which is imposed by the stirrer rotation speed. In  
this way, any excessive polymer content inside the  
reactor is avoided, with the related risks of reactor  
"blocking" or of excessive mechanical stress applied  
20 to the stirrer.

#### The process

Details on the process of the present inven-  
tion are given herebelow, with reference to fig. 1.

The polymerization reactor is indicated by  
25 number 1. The reactor outlet 12 joins the reactor to  
the discharge screw 11, which in turn is connected via  
throttle valve 13, to the double screw devolatilizer  
14. Monomers and reaction medium make-up are fed via  
lines 15, A, B and C to heat exchanger 16, where they  
30 are cooled down to polymerization temperature, and there-  
from to reactor, via line 17. The two catalyst compo-

nents are separately fed to the reactor, via lines 18A and B. As soon as the catalyst components come in contact with the monomers the polymerization takes place. Polymer particles are produced around the active centers. It has been observed with surprise that a quick withdrawal of polymer particles from the reactor (above indicated as skimming) does not influence neither the polymerization rate nor the polymer yield. The polymerization is performed at temperatures between 208 and 288K°, at pressures correspondent to the vapor pressure of the reacting system, in general between 0,1 and 4 bar. In this way the reactor content is allowed to boil. The vapors are collected in the reactor dome and then, via line 19 to the knockout drum 20, and, via line 21, sent to compressor 22. The compressed vapors are cooled and condensed in heat exchanger 23. The condensate is flashed in flash drum 24, via throttle valve 25, which drops the pressure to the same level as that of the reactor 1. In flash drum 24 a part of the condensate fed to throttle valve 25 is vaporized and recycled to knock-out drum 20, via line 26, and therefrom to compressor 22, via line 21, together with the vapors coming from the reactor, via line 19. A part of the condensate fed to throttle valve 25 is collected in flash drum 24 as a liquid, at a temperature close to that of reactor 1. This liquid is sent to the reactor under level control, via line 27. In a steady state, the vapors produced by reactor 1 are almost completely recycled to it as liquids, at a temperature close to that of the reactor. Summing up, the polymerization heat is removed from the reactor

- 9 -

as latent vaporization heat.

Any non condensable in heat exchanger 23 is  
purged via an outlet placed in the coldest part of  
5 heat exchanger 23 and sent, via line 28, to a vacuum  
pump (not shown in the figure).

The slurry produced by the reactor is concentrated, as already said, in the discharge screw 11,  
fed through throttle valve 13 to mechanical devolatilizer 14, where the residual liquids are removed, by  
10 combined thermal and mechanical action, as vapors via  
line 29. For the sake of exemplification the polymer  
concentration at the reactor outlet can be high as 50%  
wt and at the discharge screw outlet as high as 70% wt.  
15 The produced IIR shows a high MW. Number average MN's  
between 100000 and 500000 are obtained by the process  
as above described.

#### The catalysts

Suitable catalysts for the process of the  
20 present invention are the syncatalysts, which have  
been extensively patented BE 663319, BE 663320, GB  
Pat. Nos. 1362295, 1407414, 1407415, 1407416, 1407417,  
1407418, 1407419, 1407420, 1409337; The composition  
and the characteristics of said catalysts are broadly  
25 described in the mentioned patents and in several publication on this subject. (M. Baccaredda, M. Bruzzone et al Chim. e Ind. (Milano) 55,109 (1973). A characteristic of syncatalysts is the fact that the active centers are obtained by interaction of, at least,  
30 two components, in a stoichiometric ratio not lower/higher than three decades, unlike conventional Friedel-Craft catalysts, in which the co-catalyst, or co-initiator

- 10 -

tiator, is present in a very small amount, sometime  
non measurable amount. Several syncatalysts are made  
5 of just two components. The first one belongs to the  
class of Aluminium trialkyls or of Aluminium dialkyl  
monohalides, as for ex.  $\text{AlEt}_3$ ,  $\text{AlEt}_2\text{Cl}$ ,  $\text{AlEt}_2\text{Br}$ ,  
 $\text{Al}i\text{Bu}_2\text{Cl}$  etc.

Typical examples of second components of  
10 syncatalysts are : halogens, interhalogenic compounds  
and organic halides which contain at least a halogen  
atom susceptible to be exchanged with the first compo  
nent of the catalyst system in the process conditions.  
 $\text{Cl}_2$ ,  $\text{Br}_2$ , Iodine chloride, tert-butylchloride, tert-  
15 butylbromide, chloranil are non-limitative examples  
of second component of syncatalysts. The ratio between  
the two catalyst components is in general indicated by  
the atomic ratio  $\text{Al}/\text{X}$ , where X is the halogen present  
in the second component of the catalyst mixture. The  
20  $\text{Al}/\text{X}$  ratio is in general higher than 1 and can be as  
high as 1000, the preferred ratio ranging from 10 to  
300.

The consumption of second component, expres  
sed in mol per mol of polymerized monomer, is in ge  
25 neral ranging from  $1 \times 10^{-6}$  and  $50 \times 10^{-6}$ .

#### EXAMPLE

The flow sheet of the polymerization run  
of this example is show in fig. 1. The reactants  
amount, expressed in kg/h, and their temperature,  
30 expressed in  $^\circ\text{C}$ , in steady state conditions are shown  
in the attached Table. In this Table also the cross-  
reference numbers with fig. 1 are indicated.

The reactor of the experiment was the one

described in fig. 2. The reactor was insulated with polystyrene foam. A certain quantity of pure Methylchloride (MeCl) was fed as a liquid, via line 15 C, to the exchanger 16, where it was cooled to  $-45^{\circ}\text{C}$ , and therefrom to reactor 1, via line 17, up to a selected level. Isobutene and isopropene were then fed, via lines 15 A and B; in the quantity shown in the Table, and the two components of the catalyst, via lines 18 A and B. The two components were Aluminumdiethylmonochloride (DEAC)

TABLE

POINT OF ANALYSIS	Polym	MeCl	1C4 <sup>-</sup>	Isop.	T(C°)	P(kg/cm <sup>2</sup> )
17 (Feeding)		6.1	14.6	0.4	45	0.34
19 (Vapor from reactor)		20.6	4.4	0.7	45	0.34
27 (Recycle to reactor)		20.6	4.4	0.7	46	0.34
29 (Volatiles from desolv.)		6.1	2.4	0.1	100	0.20
30 (Dry polymer)	12.5	-	-	-	100	1.00

Units: kg/h

and tert-Butylchloride (TBC). Upon feeding of the two catalyst components, a milky slurry of polymer was immediately formed. The reactor temperature and pressure showed a trend to increase. The pressure increase fostered the intervention of the pressure control placed on the knock-out drum 20, and compressor 22 began to suck the reactor vapors, via line 19 and knock-out drum 20. From this moment onward the pressure in the reactor remained constant at the value of

- 12 -

5        0.34 bar, corresponding to the equilibrium temperature of  $-45^{\circ}\text{C}$  in the reactor. The other controls shown in fig. 1 were put into operation. The vapors compressed by compressor 22 were condensed in heat exchanger 23 and the condensate was expanded in vessel 24, kept  
10        at the same pressure of the reactor. The condensate was partially vaporized, with a consequent temperature drop, till to a value close to that of the reactor. The cold liquid collected in vessel 24 was sent to the reactor under level control, via line  
15        27, whereas the vapors returned to the compressor via line 26 and knock-out drum 24. In this way the vapors produced by the reactor were quantitatively recycled to the same as liquids, at a temperature close to its temperature. The polymer concentration in the reactor increased till to a steady value, at which the formed  
20        polymer was quantitatively removed by discharge screw 11. The polymer concentration at throttle valve 13 was about 60%. The polymer was fed, through valve 13 in desolventizer 14, where by combined thermal  
25        and mechanical action, the residual liquids were vaporized and recovered via line 29. The IIR free from volatiles was collected as a rubbery extrudate on a conveyor belt 30. The polymer output was about 12,5 kg/h.

30                The formation of polymer in the reactor and its removal by discharge screw 11 were decreasing the monomers concentration in the reaction medium and the polymer mass contained in the reactor. The first effect was detected by a decrease of monomers  
35        concentration in the vapors at the reactor out

5        let (line 19), controlled by an analyzer which fostered an increase of isobutene feed. In turn, this increase fostered an increase of isoprene feed, through a controller of feed ratio. The second effect was detected by a decrease of liquid level in the reactor,  
10        which fostered the intervention of the reactor level controller, which increased the MeCl feed. All fresh monomers and MeCl were cooled to  $-45\text{ C}^{\circ}$  in heat exchanger 16.

          According to the above flow sheet, the polymerization heat was removed as latent heat of vaporization, and the vapor output from the reactor was dependent on catalyst concentration inside the reactor. Consequently, the feed of one component of the catalyst system was controlled by the vapors output of  
15        the reactor. The feed of the second component of the catalyst was kept proportional to the first one by a controller of feed ratio.  
20

CLAIMS

1. A continuous process for the production of high molecular weight isobutene-isoprene copolymers, containing from 0.5 to 10wt-% of combined isoprene, said process being characterized by the contemporary presence of the following critical characteristics in the various process sections :
- i) polymerization section characterized by the fact that the copolymer is formed, and is maintained during the polymerization course, as a suspension of particles in a liquid phase, said liquid phase being composed of monomers and methylchloride, at a temperature chosen in the range between -65 and +15°C, in the presence of polymerization catalysts obtained by combination of a least two components, the first of which being selected among aluminum trialkyls and aluminum dialkylmonohalides, and the second among halogens, interhalogenic compounds, alkyl- and arylhalides, said catalyst components being fed separately to the polymerization, the polymerization temperature being kept constant by boiling the liquid phase at a pressure between 0.1 and 4,0 bar.
- ii) discharge section of the polymer slurry from the polymerization section characterized by the fact that said polymer suspension (slurry) is conveyed and compressed upwards, squeezing the liquid phase downwards, so re-fluxing it to the polymerization section.
- iii) devolatilization section characterized by the fact the concentrated polymer slurry, obtained in the preceding point ii) is transformed into a solid



5 rubbery polymer, free of volatiles, whereas the liquid phase contained in the slurry is vaporized and recovered by condensation.

2. Devices suitable for the realization of the process of claim 1), i.e.:

10 i) a tri-phasic polymerization reactor, in which a polymer phase, a liquid phase and a vapor phase are present, the last two phases being made of isobutene, isoprene and methylchloride, said reactor being provided with a stirrer as show in fig. 2, capable of homogenizing the liquid phase in every point of the condensed phase of the reactor, of conveying  
15 (skimming) the polymer phase across the reactor toward the slurry outlet, without packing the polymer in the form of a viscous mass, the vapor phase of said reactor being separated and collected by gravity in the ceiling of said reactor.

20 ii) a device for the discharge of the polymer slurry produced by the polymerization reactor, made of a vertical extruder fastened and connected to said reactor, the screw of said extruder conveying upright the polymer slurry and concentrating  
25 it by compression while allowing part of the liquid contained in the slurry to flow downward, toward the polymerization reactor, said liquids containing soluble catalyst components.

30 iii) a desolventization device of the polymer slurry coming from the discharge device of the preceding point ii), preferably a double screw extruder with heated jacket, which separates the solventized polymer, in the form of a rubbery extrudate, from

the vapors obtained by vaporization of the liquid  
5 phase contained in the slurry fed to the desolventizer.

3. A process according to claim 1, in which  
the first component of the catalyst system is chosen  
among aluminum trialkyls and aluminum dialkylmono-  
halides.

10 4. A process according to claim 1, in which  
the second component of the catalyst system is chosen  
among halogens and alkylhalides.

5. A process according to claim 1, in which  
the polymer slurry at the desolventization inlet  
15 has a solid concentration between 60 and 70wt-%.

6. Butyl rubber with a isoprene content lower  
than 5wt-% and a number average molecular weight  
between 50000 and 500000, obtained according to the  
preceding claims 1 to 5.

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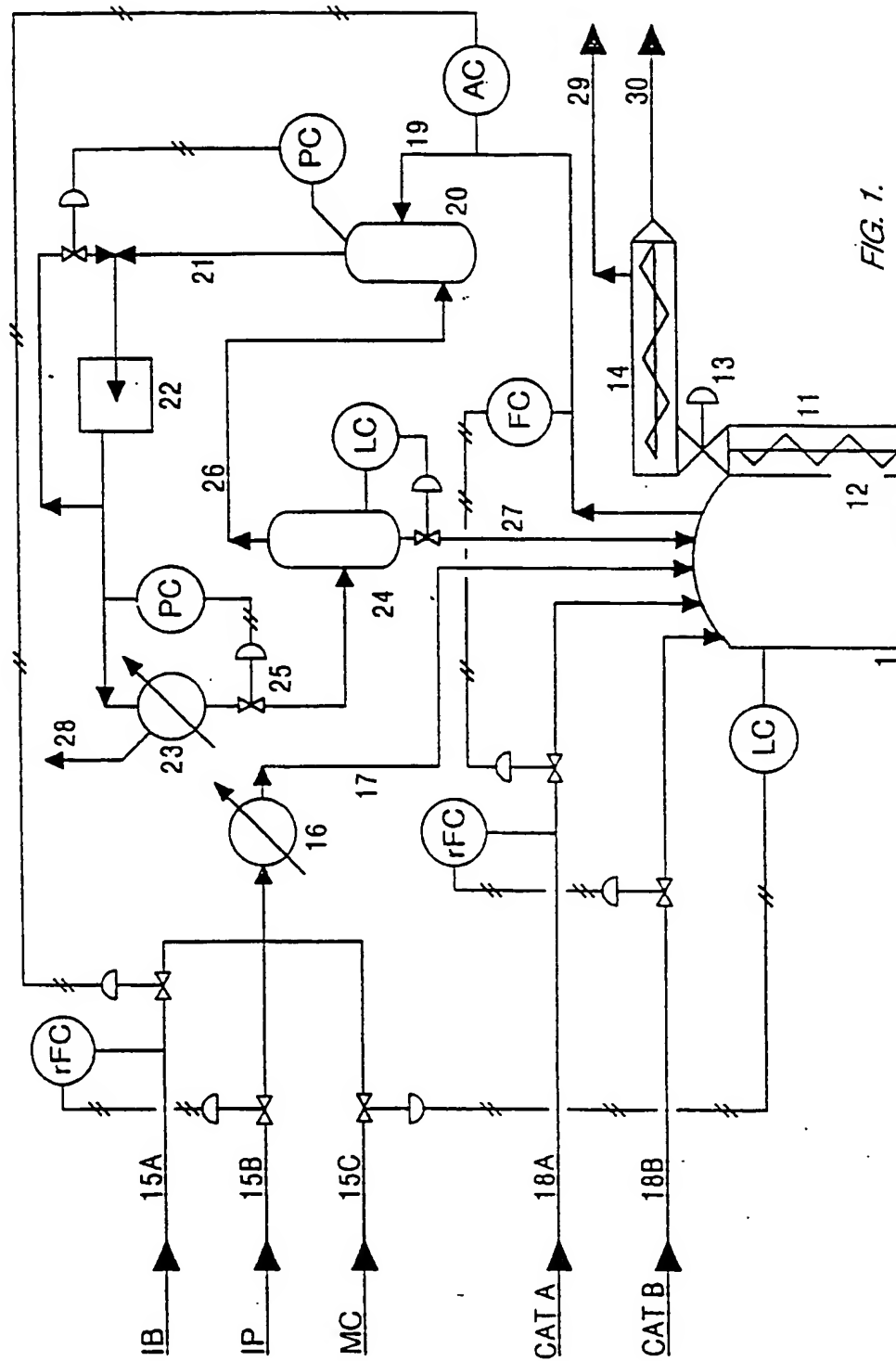


FIG. 1.

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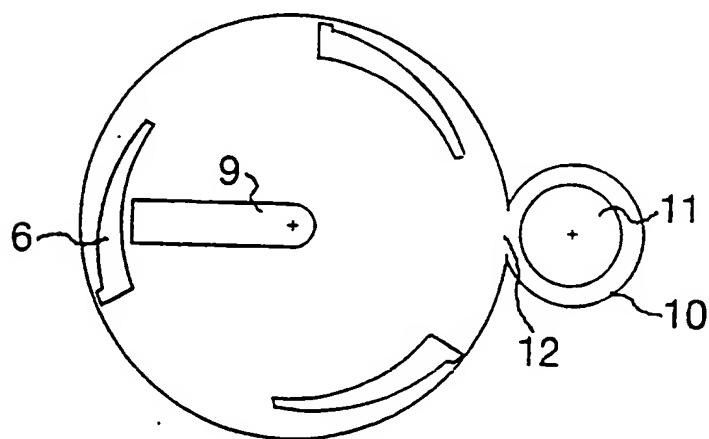
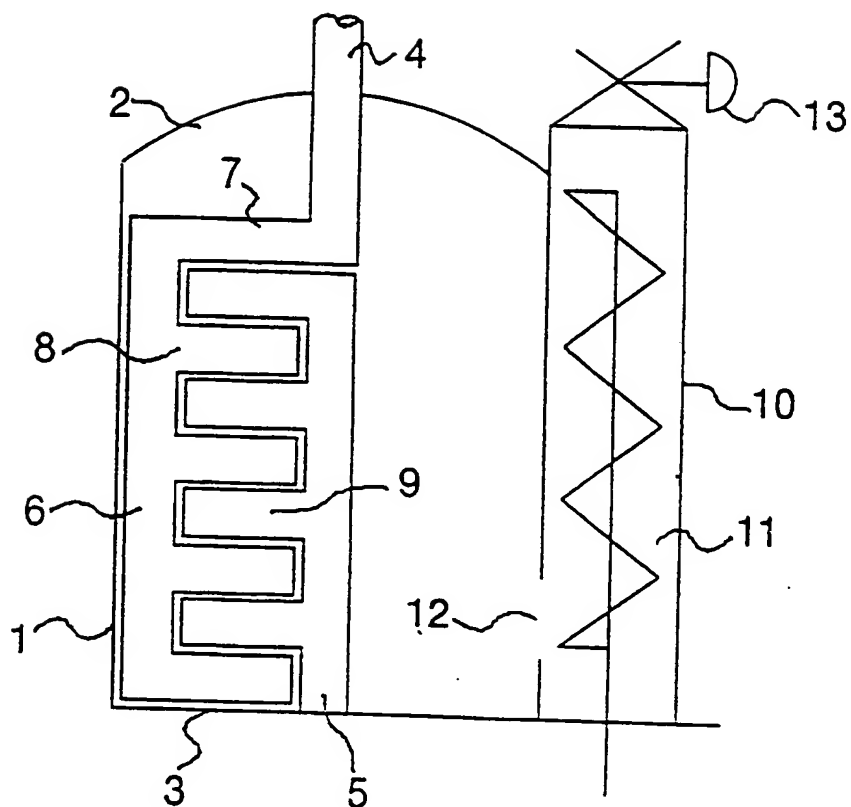


FIG. 2.

## INTERNATIONAL SEARCH REPORT

PCT/IT 93/00033

International Application No

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08F210/12; C08F2/00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C08F	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claims No. <sup>13</sup>
X	EP,A,0 209 253 (ENICHEM ELASTOMERI SRL) 21 January 1987 see the whole document	1,3,4,6
A	GB,A,561 324 (STANDARD OIL COMPANY) 15 May 1944 see claims 1-4,7	
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
17 AUGUST 1993		01.09.93
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		FISCHER B.R.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

IT 9300033  
SA 73789

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0209253	21-01-87	CA-A- 1271896 US-A- 4714747	17-07-90 22-12-87
GB-A-561324		None	

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